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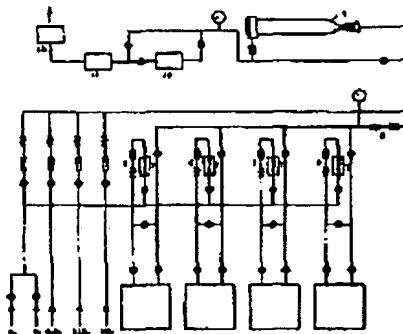
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[54]发明名称 光辐射加热金属有机化学汽相沉积氟化镓  
生长方法与装置

[57] 緒論

光辐射加热金属有机化学汽相淀积GaN的生长方法和装置,将 $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(蓝宝石)衬底进行表面清洗,然后将衬底进入采用环貌石英反应器的碘钨灯光辐射加热系统反应室内,抽真空;衬底在H<sub>2</sub>气氛下高温退火,通入TMG和NH<sub>3</sub>生长GaN缓冲层,生长GaN外延层,本发明利用光辐射促进了NH<sub>3</sub>分子分解,有利于抑制GaN外延层中的N空位,得到了近乎完美的单晶。



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## 权 利 要 求 书

1、光辐射加热金属有机化学汽相沉积 GaN 的生长方法，其特征是将 $\alpha$ -Al<sub>2</sub>O<sub>3</sub>（蓝宝石）衬底进行表面清洗，然后将衬底进入反应室抽真空（真空高于  $5.0 \times 10^{-5}$  Torr）；衬底在 H<sub>2</sub> 气氛下高温退火(1050 °C~1100 °C)，然后在 NH<sub>3</sub> 气氛下氮化(1000 °C~1050 °C)，然后通入 TMG 和 NH<sub>3</sub>，生长 GaN 缓冲层(500 °C~550 °C)，生长 GaN 外延层(900 °C~1050 °C)；GaN 外延层在 NH<sub>3</sub> 气氛下退火(900 °C~1050 °C)；降温取出样品。

2、光辐射加热金属有机化学汽相沉积 GaN 的生长装置，其特征是包括采用环绕石英反应器的碘钨灯光辐射加热系统、碘钨灯外层设有水冷却系统、机械泵和扩散泵构成的真空系统、其特征是石英反应器内设石英支架，在其上置有衬底和测温装置、还包括与石英反应器连通的气源和由电磁阀和质量流量计控制的生长气源，生长气源起码包括三甲基镓和 NH<sub>3</sub> 气体。

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## 说 明 书

## 光辐射加热金属有机化学汽相沉积氮化镓生长方法与装置

本发明涉及一种生长氮化镓(GaN)材料的方法和装置，尤其涉及利用光辐射加热金属有机化学汽相沉积氮化镓材料的生长方法与装置。

以GaN及InGaN、AlGaN合金材料为主的III-V族氮化物材料(又称GaN基材料)是近几年来国际上倍受重视的新型半导体材料。其1.9—6.2eV连续可变的直接带隙，优异的物理、化学稳定性，高饱和电子漂移速度，高击穿场强和高热导率等优越性能使其成为短波长半导体光电子器件和高频、高压、高温微电子器件制备的最优先材料。1994年底，首次出现了GaN基高亮度蓝光发光二极管(LED)，室温下工作电流20mA时，输出光功率1mW，亮度达1.2Cd；又推出绿光、白光LED，现已形成大规模生产能力。荷兰Philips公司、英国HP公司等也先后推出GaN基蓝光LED并实现商品化生产。1995年12月，日本日亚公司又研制出世界上第一只GaN基多量子阱蓝光激光二极管(LD)，室温下工作电流2.3A时，可输出417nm的脉冲激光，功率2.5mW。1996年底，该公司实现GaN基蓝光LD的室温连续波(CW)发射，寿命达20多小时，1998年6月，该公司宣布其GaN基蓝光LD的发射寿命已超过6千小时，外推寿命超过1万小时，预计98年底可推出商品。

目前，制备GaN材料的主要方法是采用金属有机化学气相沉积(MOCVD)，在蓝宝石( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>)或碳化硅(SiC)衬底上异质外延GaN单晶薄膜。GaN基材料是自然界不存在，而完全由人工制备的新型半导体材料，主要包括立方相(闪锌矿结构)和六方相(纤锌矿结构)两种结构类型。立方GaN为热力学上的亚稳相，高温下不稳定。因此，用于制备半导体器件的GaN材料主要是六方相。由于GaN的饱和N<sub>2</sub>气压很高，人们无法象拉制Si和GaAs那样在常规条件下拉制GaN单晶体材料。即使在1百多个大气压下拉制的GaN晶体直径也只有几毫米，根本不实用。因此，到目前为止，实用的GaN材料制备方法是在异质材料如 $\alpha$ -Al<sub>2</sub>O<sub>3</sub>、SiC等衬底上异质外延GaN单晶薄膜。用于GaN异质外延的方法主要有：射频加热(RF)金属有机化学气相沉积(MOCVD)，分子束外延(MBE)和卤化物汽相外延(HVPE)。其中，MOCVD是最有效和实用的外延生长方向，具有最强的工业应用背景。正是由于80年代末，90年代初用于GaN基材料生长的MOCVD外延生长技术的突破，才在国际上掀起GaN基材料和器件的研究热潮。中国专利CN94105603给出了一种快速灯加热生长锗硅异质结的方法，但其方法并不能直接用于在 $\alpha$ -Al<sub>2</sub>O<sub>3</sub>基底上生长GaN。

在MOCVD制备GaN薄膜的过程中，使用的Ga源为高纯H<sub>2</sub>或N<sub>2</sub>气体携带的金属有0机材料如三甲基镓(TMG)或三乙基镓(TEG)，N源为高纯氨气(NH<sub>3</sub>)。它们在高达1000℃以上的温度下反应，在 $\alpha$ -Al<sub>2</sub>O<sub>3</sub>或SiC等衬底上形成GaN薄膜。由于现在MOCVD技术对气压、流量、温度等的控制已达到很高的水平，加上采用了缓冲层技术等新的异质外延生长技术，用MOCVD方法制备的GaN材料质量已达到了初步实用化的水平，目前制备的

GaN 基短波长 LED 、 LD 等器件均采用 MOCVD 制备的 GaN 基材料。

用射频加热 MOCVD 制备 GaN 外延薄膜依然存在一些困难，主要包括

(1) 由于 GaN 和衬底材料的晶格失配和热失配，加上高温生长，使 GaN 外延层中的位错密度高达  $10^9$  -  $10^{10} \text{ cm}^{-2}$  量级。即使人们采用了选择横向外延技术、多层缓冲层技术等方法，位错密度依然在  $10^6 \text{ cm}^{-2}$  以上。

(2) 由于作为 N 源的 NH<sub>3</sub> 分子的离化能非常高，即使在 1000 °C 以上的生长温度下，NH<sub>3</sub> 分子分解率也低于 1%，使得 GaN 外延层中存在大量 N 空位，导致 GaN 样品呈本征 n 型。

(3) 由于作为 p 型掺杂剂的 Zn 、 Mg 原子在 GaN 禁带中的离化能达 200meV，使得 GaN 的 p 型掺杂效率很低。

(4) 由于作为 Ga 源的 TMG 与 NH<sub>3</sub> 在较低的温度下就会产生寄生反应，反应物作为杂质或缺陷存在于 GaN 外延层中。这已公认是 GaN 外延层的发光谱存在“黄带”的重要原因。而“黄带”发射越强，表示 GaN 材料的质量越差。

以上困难的存在，影响到制造高质量的材料和器件，也制约了 GaN 材料生长和器件研制的进一步发展。

为了解决用 MOCVD 方法制备 GaN 外延薄膜存在的问题，世界各国的科学家尽了很大的努力。为了减低 GaN 外延层中的 N 空位，人们的努力可主要归结于两个方面：(1)对 MOCVD 材料生长系统进行改进，最典型的是用电子回旋共振(ECR)形成等离子体来活化 NH<sub>3</sub> 分子，可大大提高 NH<sub>3</sub> 分子的分解效率，降低生长温度，不仅可减低 GaN 层的 N 空位浓度，对减少位错密度也有帮助。但 ECR 技术本身是一门非常专门的技术，存在着技术复杂、投资大、体积庞大、电磁干扰严重等缺点。(2)寻找新的 N 源，如采用 hydrazine(肼氮)等有机氮源。这方面的努力尚未成功，主要是在提高了活化 N 源的同时，带来了更严重的寄生反。

本发明的目的是：提供一种光辐射加热金属有机化学汽相沉积 GaN 生长方法，改善材料质量，提出一种可用于器件的材料的制备方法，促进 GaN 材料生长和器件研制的进一步发展。

本发明的目的还在于提供一种光辐射加热金属有机化学汽相沉积 GaN 的生长装置。

本发明的技术方案是，建立专用于 GaN 材料外延生长的光辐射加热低压 (MOCVD) 系统。在该系统中，包括采用环绕石英反应器的碘钨灯光辐射加热系统代替一般 MOCVD 系统中普遍采用的 RF 射频加热。石英反应器内设石英支架，在其上置有衬底和测温装置。石英反应器连通由电磁阀和质量流量计控制的生长气源，生长源包括三甲基镓和 NH<sub>3</sub> 气体等。整个系统由机器泵和扩散泵构成的真空系统保证真空和在生长材料过程中维持低压。

本发明的工艺方法为：将  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (蓝宝石) 衬底进行表面清洗，然后将衬底进入反应

室抽真空(真空度高于  $5.0 \times 10^{-5}$  Torr)；衬底在  $H_2$  气氛下高温退火(1050 °C–1100 °C)，然后在  $NH_3$  气氛下氮化(1000 °C–1050 °C)，然后通入 TMG 和  $NH_3$  生长 GaN 缓冲层(500 °C–550 °C)，生长 GaN 外延层(900 °C–1050 °C)；GaN 外延层在  $NH_3$  气氛下退火(900 °C–1050 °C)；降温取出样品。

本发明的特点是：本发明的装置具有投资小、设备简单、体积小、无电磁干扰、系统设备稳定可靠、自动控制精度高、操作方便等特点。采用该生长系统，在  $\alpha$ - $Al_2O_3$  衬底上制备出 GaN 单晶薄膜，通过双晶 X 射线摇摆曲线、光荧光谱和霍尔测量等表征方法均证明 GaN 外延层具有很高质量，特别是 950 °C 下生长出的 GaN 层在室温下未观察到“黄带发射”。

本发明建立的光辐射加热 MOCVD 系统制备 GaN 材料的过程中，首先采用光辐射加热代替一般的 RF 射频加热，对解决上述第 2 和第 4 个困难具有良好效果。

从 GaN 材料制备机理上，光辐射加热具有下述两点作用：

(1)光辐射促进了  $NH_3$  分子分解，有利于抑制 GaN 外延层中的 N 空位。

$NH_3$  分子中 N-H 键的键能是 3.676eV，对应于波长 337.3mm 的紫外光。图 3 是我们测试的碘钨灯发光谱，从中可以看到光谱包括了这部分能量的光子，甚至更高能量的光子。因此，光辐射可提高  $NH_3$  的分解效率。

(2)抑制 TMG 和  $NH_3$  之间的寄生反应，促进寄生反应物的分解。

TMG 和  $NH_3$  寄生反应产物一般为含 C 的杂质，夹带于 GaN 外延层中，不仅作为杂质影响 GaN 的性质，而且会引起其它缺陷，如层错等。因此，如果 GaN 生长温度低于 950 °C，寄生反应严重时，GaN 薄膜呈黄色。即使高温下制备的样品也会在其发光谱上 550nm 左右形成较宽的峰包，即“黄带”。

我们采用自行设计、建立的光辐射加热 MOCVD 材料生长系统在  $\alpha$ - $Al_2O_3$  衬底上成功地制备了高质量 GaN 单晶薄膜。实验证明采用光辐射加热代替 RF 射频加热，取得了非常好的效果。特别是在生长温度 950 °C 时，制备出无“黄带”发射的 GaN 外延层，这在国际上是首次，无疑与光辐射的作用有关。并列出了一组用光辐射加热 MOCVD 系统制备的 GaN 外延薄膜的表征结果。

但是在光辐射加热的条件下，900 °C 生长的样品就呈现无色透明，950 °C 生长的样品，发光谱上观察不到“黄带”发射。而国外用 RF 射频加热的 MOCVD 系统生长的 GaN 薄膜，生长温度 1050 °C 时，也有较强的“黄带”发射。

从机理上看，这是因为光辐射抑制了寄生反应，并促进了寄生反应物的分解，使 GaN 层中杂质 C 原子外溢，形成  $CH_4$  气体排出反应室外。因此，用光辐射加热代替 RF 射频加热对解决上述第(2)和第(4)个问题具有一定的效果。

以下结合附图和通过实施例对本发明作进一步说明：

图 1 是本发明系统示意图，除了具有一般 MOCVD 系统所具有的对气压、流量、温度

的高精度控制外，该系统最大的特点是采用光辐射加热代替了一般 MOCVD 系统采用的高频感应(RF)加热。

图 2 所示，本发明光加热装置结构示意图(图 2a)，图 2b 为加热器横向剖视图。图中由 18 根环绕石英管反应器的碘钨灯组成，每根功率 1KW，其发射光强由自行设计的可控硅电路控制，因此，发光强度及反应器内的温度都可由计算机进行自动控制。

图 3 为本发明碘钨灯发光光谱图，图中横向联合座标为波长，纵座标表示发光强度，且为一相对强度单位。

图 4(a)是本发明  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 村底上 GaN 外延层的 X 射线衍射谱(XRD)，位于 34.0° 和 72.7° 的衍射峰，分别来自于 GaN(0002)和(0004)晶面的衍射。除此之外，没有任何来自于其他晶面的衍射峰，说明 GaN 外延层只有一个晶面取向。图 4(b)是 GaN(0002)衍射峰的 X 射线双晶摇摆曲线，其半高宽(FWHM)为 8.7 分(arcmin)，说明 GaN 外延层是晶体结构非常完整的单晶薄膜。图中横座标为衍射角度，纵座标为相对强度。

图 5 是本发明 GaN 外延层的透射光吸收谱，横座标为波长，纵座标为透射率，在 365nm 附近，可以看到非常陡峭的光吸收边。据此测定的 GaN 外延层禁带宽度为 3.4eV，与室温下 GaN 禁带宽度的标准值相等。

图 6 是本发明 GaN 外延层分别在室温和低温下测量的光荧光谱(PL)，横座标为波长，纵座标为光荧光相对强度，位于 367nm 的发射峰代表了 GaN 的带边发射，其强度越高，说明 GaN 层的光学质量越好。同时，我们在室温和低温下都观察不到位于 550nm 左右的“黄带”发射，说明外延层中与“黄带”有关的缺陷或杂质密度很低。PL 谱测量结果说明 GaN 外延层具有很好的光学质量。图 6(a)为在室温下测量，图 6(b)为在 10 K 的温度下测量。

#### 材料制备方法：

1.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (蓝宝石) 村底进行表面清洗
2. 村底进入反应壳抽真空 (真空度高于  $5.0 \times 10^{-5}$  Torr)
3. 村底在 H<sub>2</sub> 气氛下高温退火(1050 °C)
4. 村底在 NH<sub>3</sub> 气氛下氮化(1050 °C)
5. 生长 GaN 缓冲层(520 °C)，接通 Ga 源，以 H<sub>2</sub> 将 TMG 或 TEG 带出。
6. 升温退火(900 °C—1050 °C，根据外延层生长要求改变升温速率和退火温度)
7. 生长 GaN 外延层
8. GaN 外延层气氛下退火(1050 °C)
9. 降温取出样品

用范得堡法进行的室温霍尔(Hall)测量显示 GaN 外延层在室温下 n 型背景载流子浓度是  $10 \times 10^{16} \text{ cm}^{-3}$ ，霍尔迁移率为  $121.5 \text{ cm}^2 / \text{V.S.}$ 。上述结构、光学、电学测量结果均表

明用我们自行设计、建立的光辐射加热 MOCVD 生长系统制备的 GaN 外延层是高质量的 GaN 单晶薄膜。在用 MOCVD 方法制备 GaN 基材料的过程中，采用光辐射加热代替一般的 RF 射频加热取得了很好的使用效果。其余测量结果在图中均有给出。

图 1 和图 2 所给出的用于 GaN 材料外延生长的光辐射加热低压 (MOCVD) 装置，在该装置的实施例中，包括采用环绕石英反应器 1 的碘钨灯 2 构成的确光辐射加热系统，以此代替一般 MOCVD 系统中普遍采用的 RF 射频加热。碘钨灯 2 的周围设有冷却水 13，以保证不锈钢炉体不变形。石英反应器内设有石英支架 3，在其上置有衬底 4 和测温装置 5、石英反应器连通由电磁阀 6 和质量流量计 7 控制的生长气源，生长源包括三甲基镓 8 和 NH<sub>3</sub> 气源 9 等，图 1 中有 4 路生长气源，可用有机铟源、有机铝源等。整个系统由机器泵 10 和扩散泵 11 构成的真空系统保证真空和在生长材料过程中维持低压。机器泵 10 和扩散泵 11 排出的气体经过一废气处理装置 12 再排到大气。图中还有构成的管道、针阀、压力表、浮子流量计等。

1988-11-19

说 明 书 附 图

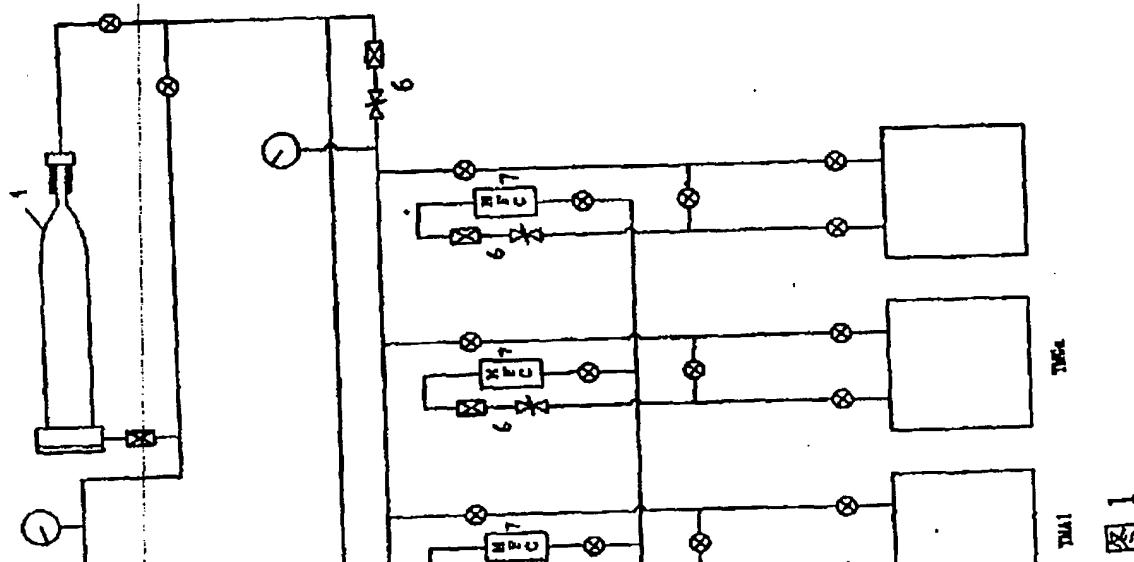


图 1

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[54] Name of invention: A light radiation MOCVD Gallium Nitride generation method and installation

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[57] Abstract: A light radiation heated MOCVD gallium nitride (GaN) generation method and installation, involving cleansing of the surface of an $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (sapphire) substrate, then introduction of the substrate to an iodine tungsten light radiation heating system quartz ring reactor chamber, then creation of a vacuum; high temperature annealing of the substrate then takes place in an H<sub>2</sub> atmosphere, then TMG and NH<sub>3</sub> are introduced generating a GaN buffer layer, then generation of the GaN epitaxial layer; the use of light radiation by this invention accelerates the decomposition of NH<sub>3</sub> molecules, which is beneficial in suppressing the generation of N vacancies in the GaN epitaxial layer, yielding virtually perfect single crystals.

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## CLAIMS

1. The light radiation heated MOCVD GaN generation method, wherein this involves cleansing of the surface of an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (sapphire) substrate, then introduction of the substrate to a reaction chamber and introduction of a vacuum (vacuum higher than  $5.0 \times 10^{-5}$  Torr); then annealing (1050-1100°C) of the substrate in an H<sub>2</sub> atmosphere, then amination (1000-1050°C) in an NH<sub>3</sub> atmosphere, then introduction of TMG and NH<sub>3</sub> generating the GaN buffer layer (500-550°C), then generation of the GaN epitaxial layer (900-1050°C); the GaN epitaxial layer then being annealed (900-1050°C) in an NH<sub>3</sub> atmosphere; the temperature then being lowered to take out the sample.
2. The light radiation heated MOCVD GaN generation installation, wherein this includes the use of a quartz ring reactor iodine tungsten light radiation heating system, the outer layer of the iodine tungsten light having a water cooling system, and a mechanical pump and diffusion pump vacuum system, wherein the quartz reactor is fitted with an internal quartz stand, on which are located the substrate and temperature sensors, whilst also including gas sources connected to the quartz reactor with generating gas sources controlled by electro magnetic valves and mass flow metres, the generating gas sources being at least TMG and NH<sub>3</sub> gasses.

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## DESCRIPTION

### A light radiation heated MOCVD Gallium Nitride generation method and installation

This invention relates to a type of method and installation for the generation of gallium nitride (GaN) materials, particularly it relates to a light radiation heated MOCVD gallium nitride generation method and installation.

Class III-V nitride materials (also known as GaN base materials) mainly based on GaN and InGaN and AlGaN alloys are a semiconductor material that has attracted much international attention in the last few years. Its 1.9 -6.2eV continuous variable direct band gap, excellent physical and chemical stability characteristics, high saturation electron source migration speed, high break down electric field strength and high heat conductivity characteristics have made it the material of preference in the construction of short wavelength semiconductor photo electronic and high frequency, high voltage, high temperature laser electronics components. At the end of 1994, high luminosity blue light LEDs based on GaN first appeared, and these had a light output power of 1mW with a luminosity of 1.2Cd at room temperature with a working current of 20mA. Green light and white light LEDs were also developed, and these are already in high capacity production. Philips of Holland and HP of the USA also presented blue light LEDs based on GaN at various stages and have achieved commercial production. In December of 1995, Nichia of Japan also developed the world's first LD based on GaN which when working at room temperature at a current of 2.3A was capable of outputting 417nm laser pulses at a power of 2.5mW. At the end of 1996, that company also developed room temperature CW emission using a blue light LD based on GaN, having a service life of over 20 hours, and in June 1998, they announced that the service life of the GaN based blue light LD emission already exceeded 6000 hours, with service life expected to reach 10,000 hours, it being expected that they will be able to release this product around the end of 1998.

Currently, the main method of producing GaN materials involves MOCVD, with epitaxial growth of a single crystal GaN membrane taking place on a Sapphire ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) or silicon carbide (SiC) substrate. GaN materials do not exist naturally, they are a completely artificial new type of semi-conductor material, mainly consisting of cubic phase (zinc blend structures) and hexagonal phase (wurtzite structures) structures. Cubic GaN in terms of thermodynamics is a metastable phase, being unstable at high temperatures. Due to this, GaN materials for use in construction of semiconductor components mainly employ hexagonal phase. As the saturated gas pressure of N<sub>2</sub> in GaN is very high, nobody has been able to pull GaN single crystal materials under normal conditions in the same way as Si and GaAs. Even under a pressure of over 100 atmospheres, it is only possible to pull a GaN single crystal with a diameter of a few millimetres, which is of no use. Due to this, the GaN material manufacturing methods used so far have involved epitaxis of a GaN single crystal membrane on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, SiC or other such substrate. The main methods for epitaxis of GaN are: RF heating MOCVD, MBE and HVPE. Of these, MOCVD is the most effective and easily applied epitaxial method, and presents the greatest possibilities in terms of industrial applications. In fact it is only as a result of the breakthroughs made relating to MOCVD GaN epitaxis technology at the end of the 80s and beginning of the 90s that such attention has been paid

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internationally to the development of GaN materials and components. Chinese patent CN94105603 presented a type of rapid lamp heated germanium-silicon epitaxis method, but this method could not be used directly on an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrate for generation of GaN.

During the MOCVD GaN membrane generation process, Ga source high purity H<sub>2</sub> or N<sub>2</sub> gas carrying metals include TMG and TEG 0-ganic materials [*translator's note: term in Chinese is 0 or O followed by the second character of "organic" hence this term, correct term for this class of materials could not be ascertained*], the N source being high purity NH<sub>3</sub>. These react after reaching temperatures over 1000°C, forming a GaN membrane on an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, SiC or other such substrate. As the MOCVD technology is already advanced in terms of control of pressurisation, flow and temperature, coupled with its use of buffer layer technology and other such epitaxial growth technology, the quality of GaN materials produced using MOCVD has already reached a level allowing its preliminary adoption, and currently all short wavelength LED, LD and other such components rely on MOCVD production of GaN materials.

However there are still difficulties in the usage of RF heated MOCVD in production of GaN epitaxial membranes, mainly being:

- (1) Due to lattice mismatches between GaN and the substrate and thermal differences and high temperature for generation, the density of GaN epitaxial dislocations reaches  $10^9$ - $10^{10}$  cm<sup>-2</sup>. Even if lateral epitaxis and multi-layer buffer techniques are employed, the level of dislocations is still higher than  $10^6$  cm<sup>-2</sup>.
- (2) As the ionic energy of the NH<sub>3</sub> N source molecules is extremely high, when operating at generating temperatures of over 1000°C, the NH<sub>3</sub> molecule decomposition rate is less than 1%, with the result that large numbers of N vacancies occur in the GaN epitaxis, the GaN sample taking on latent n type characteristics.
- (3) The ionic energy of the Zn and Mg atoms of the P type adulterant within the GaN forbidden band can reach 200 meV, with the result that the effectiveness of the GaN p type adulterant is very low.
- (4) As a parasitic reaction occurs between the TMG Ga source and NH<sub>3</sub> at relatively low temperatures, the product of the reaction exists as an impurity or defect in the GaN epitaxis. This has already been recognised as the main reason for a "yellow band" occurring within the spectrum of the GaN epitaxis. The stronger the "yellow band" transmission is, the poorer the quality of the GaN material.

The existence of the above difficulties impinges on the ability to manufacture high quality materials and components, and restricts the advances that could be made in generation of GaN materials and development of components.

Internationally, enormous efforts are being made to resolve the problems surrounding the MOCVD method of preparation of GaN epitaxial membranes. The main efforts made in seeking to reduce the number of N vacancies in the GaN epitaxis fall under two categories: (1) Improvements to the

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MOCVD materials generation system, the most common being the use of ECR to create a plasma body capable of activating NH<sub>3</sub> molecules, resulting in a major increase in the NH<sub>3</sub> decomposition rate, reducing the generation temperature, thus not only reducing the concentration of N vacancies in the GaN layer, but also being useful in reducing the density of dislocations. However ECR technology is itself a very specialised field, being technically complex, costly and space consuming whilst resulting in major electro-magnetic interference. (2) The search for a new N source, for instance using hydrazine and other such organic ammonia sources. Efforts in this area have not as yet been successful, mainly due to the fact that at the same time as N activation is enhanced, even more severe parasitic effects are encountered.

The aims of this invention are: to provide a light radiation heated MOCVD GaN generation method, to improve material quality, whilst presenting a production method for use with component materials, in order to accelerate the generation of GaN materials and the development of components.

The aims of this invention are also to provide a light radiation heated MOCVD GaN generation installation.

The technical scheme of this invention being, the creation of a light radiation heated MOCVD system for the purpose of GaN material epitaxial generation. The system adopting an iodine tungsten light radiation heating system quartz ring reactor to replace the RF heating usually used in basic MOCVD systems. There is a quartz stand within the quartz reactor, on which are located the substrate and temperature sensors, whilst also including gas sources connected to the quartz reactor with generating gas sources controlled by electro magnetic valves and mass flow metres, the generating gas sources being including TMG and NH<sub>3</sub> gasses. A mechanical pump and diffusion pump vacuum system guarantees that the whole system is kept at low pressure during the generation process.

The technique used by this invention involves cleansing of the surface of an $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (sapphire) substrate, then introduction of the substrate to the reaction chamber under a vacuum (vacuum higher than 5.0x10<sup>-5</sup>Torr); then annealing (1050-1100°C) of the substrate in an H<sub>2</sub> atmosphere, then amination (1000-1050°C) in an NH<sub>3</sub> atmosphere, then introduction of TMG and NH<sub>3</sub> generating the GaN buffer layer (500-550°C), then generation of the GaN epitaxial layer (900-1050°C); the GaN epitaxial layer then being annealed (900-1050°C) in an NH<sub>3</sub> atmosphere; the temperature then being lowered to take out the sample.

This invention possesses the following characteristics: the installation represented by this invention requires low levels of investment, the equipment being simple, small in scale and without electro-magnetic interference, whilst the system equipment is stable and reliable, being highly automated and easily operated. This generation system is used to produce GaN single crystal membranes on an $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrate. Bimorph X ray rocking curve, photoluminescence and Hall measurement token methods all demonstrate that the GaN epitaxial layer is of a very high quality. This is particularly so with the GaN layer generated at 950°C which demonstrates no “yellow band emission” at room temperature.

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During the GaN material production process involving the light radiation heated MOCVD system to which this invention relates, the adoption of light radiation heating as opposed to the usual RF heating is an effective approach to resolving the difficulties associated with items (2) and (4) above.

From the point of view of the mechanisms involved in the production of GaN materials, light radiation heating has the following two effects.

(1) Light radiation accelerates the decomposition of the  $\text{NH}_3$  molecules, and this is an effective method of suppressing the N vacancies within the GaN epitaxis.

The bond energy of the N-H bond in the  $\text{NH}_3$  molecule is 3.676eV, corresponding to ultra-violet light with a wavelength of 337.3nm. Diagram 3 is the tungsten iodine lamp radiation spectrum that we measured, and it can be noted that the spectrum includes photons with this energy, and there are photons with even higher levels of energy. Therefore it can be seen that light radiation increases the  $\text{NH}_3$  decomposition rate.

(2) Suppression of the parasitic reactions between TMG and  $\text{NH}_3$  accelerates the decomposition of parasitic reagents.

The products of the parasitic reaction between TMG and  $\text{NH}_3$  are generally impurities containing C, these are carried within the GaN epitaxis, and such impurities not only affect the GaN characteristics but can also cause other defects, such as stacking faults. For this reason, if the GaN generation temperature is lower than 950°C, when the parasitic reactions are most severe, the GaN membrane becomes yellow in colour. Peak envelopes can occur in the 550nm spectrum even in samples produced at higher temperatures, thus presenting a “yellow band”.

The light radiation heated MOCVD materials generation system that we have designed and put into practice is capable of successfully producing high quality GaN single crystal membranes on an  $\text{Al}_2\text{O}_3$  substrate. Research demonstrates that the use of light radiation heating to replace RF heating yields excellent results. In particular, at generation temperatures of 950°C, a GaN epitaxis can be produced without a “yellow band” transmission, this is the first time this has been achieved internationally, and there is no doubt that this is connected with the effects of light radiation. At the same time this offers representative results for GaN epitaxis membranes produced by light radiation heated MOCVD systems.

Although under light radiated heat conditions, the samples generated at 900°C were clear and colourless, whilst samples generated at 950°C exhibited no “yellow band” spectrum, the GaN membranes generated overseas using RF heated MOCVD systems at a generation temperature of 1050°C did exhibit relatively strong “yellow band” transmissions.

In terms of the mechanisms involved, this is because light radiation suppresses the parasitic reaction, accelerating the decomposition of the parasitic reagents, with the result that the C atom impurities are expelled from the GaN layer, forming  $\text{CH}_4$  which is then expelled from the reaction chamber.

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For this reason, the use of light radiation heating to replace RF heating plays a role in resolving the problems outlined in (2) and (4) above.

The following is a more detailed description of this invention based on practical implementations and the appended diagrams:

Diagram 1 is a sketch of the system to which this invention relates, and apart from possessing highly accurate pressure, flow and temperature controls normally expected in an MOCVD system, the most outstanding characteristic is that this system relies on light radiation heating to replace the RF heating usually encountered in MOCVD systems.

Diagram 2 displays the optical heating unit presented by this invention (diagram 2a), diagram 2b is a horizontal cut-away view of the heater. This is composed of 18 quartz ring reactor tungsten iodine lamp tubes, each having a power of 1KW, the radiation strength of these is controlled by a silicon electric circuit designed by ourselves, as a result, the radiation strength and the temperature within the reactor can be controlled by computer.

Diagram 3 is the spectrum chart of the tungsten iodine lamp presented by this invention, the horizontal scale being wavelength, the vertical scale being radiation strength, showing relative strength units.

Diagram 4 (a) is the XRD of the GaN epitaxis on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrate to which this invention relates, the diffractive peaks at 34.0° and 72.7° are those diffracted from the GaN (0002) and (0004) crystal planes respectively. Apart from this, there are no diffractive peaks from other crystal planes, indicating that the GaN epitaxis possesses a crystal plane in only one direction.

Diagram 4 (b) is the bimorph X ray rocking curve of the diffraction peak of GaN (0002), its FWHM being 8.7 (arcmin), indicating that the GaN epitaxis is a single crystal membrane with a very complete crystal structure. In the diagram the horizontal scale is the diffraction angle, the vertical scale being relative strength.

Diagram 5 is the transmitted absorption spectrum of the GaN epitaxis to which this invention relates, the horizontal scale being wavelength, the vertical scale being transmitted intensity rate, at around 365nm one can see a very sharp light absorption boundary. Based on this the GaN epitaxis forbidden band is determined as 3.4eV, which is equivalent to the standard GaN forbidden band at room temperature.

Diagram 6 is the PL of the GaN epitaxis to which this invention relates measured at room and low temperatures, the horizontal scale being wavelength, the vertical scale being relative strength of PL, the emission peak at 367nm represents the GaN band edge emission, increasing strength indicating increasing optical quality of the GaN layer. In addition, we were unable to observe a “yellow band” emission around 550nm at both room and low temperatures, indicating that the density of defects or impurities within the epitaxis connected with “yellow band” are very low indeed. PL spectrum measurement results indicate that the GaN epitaxis is of excellent optical quality. Diagram 6 (a) is

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the measurement at room temperature, diagram 6 (b) is the measurement at a temperature of 10K.

**Method of producing the material:**

1. Cleansing of the surface of an $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (sapphire) substrate
2. Introduction of the substrate to a reaction chamber and introduction of a vacuum (vacuum higher than 5.0x10<sup>-5</sup>Torr)
3. Annealing (1050°C) of the substrate in an H<sub>2</sub> atmosphere.
4. Amination (1050°C) of the substrate in an NH<sub>3</sub> atmosphere.
5. Generation of the GaN buffer layer (520°C), opening of the Ga source, H<sub>2</sub> carrying either TMG or TEG
6. Raising of the temperature to carry out annealing (900-1050°C, the rate at which the temperature is raised and the annealing temperature being varied according to the epitaxis generation requirements)
7. Generation of the GaN epitaxis.
8. Atmospheric annealing of the GaN epitaxis (1050°C).
9. Temperature reduction to remove sample.

Using the Vanderbilt method to carry out Hall measurement at room temperature shows that the n type background charge carrier concentration of the GaN epitaxis at room temperature is 10 x 10<sup>18</sup>cm<sup>-3</sup>, whilst the Hall transference rate was 121.5cm<sup>2</sup>/V.S. The above mentioned structures, optics and electrical measurement results all indicate that the GaN epitaxis produced using the light radiation heated MOCVD materials generation system that we have designed yields a high quality GaN single crystal membrane. In the MOCVD process of producing GaN materials, the use of light radiation heating to replace RF heating also gave successful results. All other measurement results are also included in the diagrams.

The light radiation heated MOCVD installation used in the generation of GaN material epitaxial layers shown in diagrams 1 and 2, as indicated in this practical implementation, consists of a quartz ring reactor 1 the tungsten iodine lamp 2 of which constitutes a light radiation heating system, this being used to replace the RF heating generally encountered in MOCVD systems. The tungsten iodine lamp 2 being surrounded by coolant water 13, ensuring that the stainless steel lamp body does not warp. There is a quartz stand 3 within the quartz reactor, on top of which there are a substrate 4 and a temperature sensor 5, the quartz reactor is connected to an electro-magnetic valve 6 and a mass flow metre 7 which control the generation gas source, the generation source consisting of TMG 8 and NH<sub>3</sub> 9 gas sources, in diagram 1 there are 4 generation gas source circuits, allowing use of an organic indium source and an organic aluminium source etc. A mechanical pump 10 and a diffusion pump 11 vacuum system guaranteeing that the whole system is kept at low pressure during the generation process. The gas expelled by the mechanical pump 10 and the diffusion pump 11 passes through a waste gas processing system 12 and is then expelled into the atmosphere. There is also pipe work, needle valves, pressure gauges, and float flow metres depicted in the diagrams.

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**DIAGRAMS APPENDED TO DESCRIPTION**

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